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TITLE: PROCESS TO MANUFACTURE HIGH VISCOSITY
HYDROCRACKED BASE OILS

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PROVISIONAL APPLICATION FOR UNITED STATES PATENT

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PROCESS TO MANUFACTURE HIGH VISCOSITY HYDROCRACKED BASE OILS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims benefit of U.S. provisional patent application serial number 60/476,665 filed June 6, 2003.

FIELD OF THE INVENTION

[0002] The instant invention relates to a process to produce base oils. More particularly, the instant invention relates to a process that produces base oils through the use of fractionation, solvent extraction, dewaxing, and hydrofinishing.

BACKGROUND OF THE INVENTION

[0003] It has long been recognized that one of the most valuable products generated through the refining of crude mineral oils is lubricating oils. It is common practice to recover lubricating oil basestocks by solvent extracting, with a selective solvent, undesirable components such as sulfur compounds, oxygenated compounds, and aromatics from straight distillates. However, with the decline in the availability of paraffinic base crudes, and a corresponding increase in the proportion of naphthenic and asphaltic base crudes, it is becoming increasingly difficult to meet the demand for lubricating oil basestocks, or base oils.

[0004] Many processes have been proposed for producing lubricating oil basestocks, or base oils, from the increasing proportion of naphthenic and asphaltic base crudes. United States Patent Number 5,171,422, Kirker et al., and United States Patent Number 6,217,747 B1, Chang et al., teach a process whereby a high quality lubricating oil basestock is produced. The process involves subjecting a high boiling hydrocarbon stream to hydrocracking

conditions. The '422 patent utilizes a high silica content zeolite catalyst of the faujasite type to produce a hydrocrackate product, and the '747 patent utilizes a hydrocracking catalyst comprising a hydrogenation/dehydrogenation component and an acidic solid component modified with an oxyanion to produce a hydrocrackate product. The hydrocrackate product is then processed to produce a lubricating oil basestock.

[0005] However, there still exists a need in the art for an effective process to produce lubricating oil basestocks, or base oils, from the increasing proportion of naphthenic and asphaltic base crudes.

SUMMARY OF THE INVENTION

[0006] The instant invention is directed at a process for producing base oils. The process comprises:

- a) contacting a hydrocarbonaceous feedstock with a hydrocracking catalyst under effective hydrocracking conditions to produce a hydrocracked product;
- b) fractionating said hydrocracked product to produce at least a first bottoms fraction;
- c) contacting said first bottoms fraction with an extraction solvent to produce at least an aromatics-rich extract solution and an aromatics-lean raffinate solution;
- d) removing at least a portion of said extraction solvent from said aromatics-lean raffinate solution to produce at least an aromatics-lean raffinate;
- e) dewaxing said aromatics-lean raffinate to produce a dewaxed product;
- f) fractionating said dewaxed product to produce at least a second bottoms fraction; and
- g) hydrofinishing said second bottoms fraction to produce at least one base oil.

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0007] The present invention is a process to produce at least one base oil. The instant process involves contacting a hydrocarbonaceous feedstock with a suitable hydrocracking catalyst under effective hydrocracking conditions to produce a hydrocracked product. The hydrocracked product is then fractionated to produce at least a first bottoms fraction. The first bottoms fraction is solvent extracted, and the resulting aromatics-lean raffinate solution is processed to remove at least a portion of the extraction solvent present in the aromatics-lean raffinate solution. The removal of at least a portion of the extraction solvent from the aromatics-lean raffinate solution produces an aromatics-lean raffinate that is subsequently dewaxed. The dewaxing of the aromatics-lean raffinate produces a dewaxed product. The dewaxed product is then fractionated to produce at least a second bottoms fraction that is subsequently hydrofinished under effective hydrofinishing conditions to produce at least one base oil. The present invention gives the practitioner the ability to produce high viscosity base oils while not having to directly dewax these high viscosity base oils.

[0008] It should be noted that the phrases "aromatics-lean raffinate solution" and "aromatics-rich extract solution" are not synonymous with the phrases "aromatics-lean raffinate" and "aromatics-rich extract". The phrases "aromatics-lean raffinate solution" and "aromatics-rich extract solution" are meant to refer to the products of solvent extraction before the solvent has been removed, i.e. distilled or stripped, from the respective phases. Thus, the phrases "aromatics-lean raffinate" and "aromatics-rich extract" refer to the respective products after at least a portion of the solvent contained in the "aromatics-lean raffinate solution" and "aromatics-rich extract solution" has been removed.

[0009] The hydrocarbonaceous feedstocks suitable for use in the process of the present invention are wax-containing feedstocks that boil in the lubricating oil range. These streams typically have a 10% distillation point greater than 650°F (343°C), measured by ASTM D 86 or ASTM 2887, and are derived from mineral or synthetic sources. The wax content of the hydrocarbonaceous feedstock used herein is typically at least about 50 wt.%, based on the hydrocarbonaceous feedstock, but can range up to 100 wt.% wax. The paraffin content, of a feedstock may be determined by nuclear magnetic resonance spectroscopy (ASTM D5292) or correlative methods (ASTM D3238). Hydrocarbonaceous feedstocks having a high wax content typically have high viscosity indexes of up to 200 or more. The hydrocarbonaceous feedstocks used herein can be derived from a number of sources such as oils derived from solvent refining processes. These oils include, for example, raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, and Fischer-Tropsch waxes. Preferred feeds are slack waxes and Fischer-Tropsch waxes. Slack waxes are typically derived from hydrocarbon feeds by solvent or propane dewaxing. Slack waxes contain some residual oil and are typically deoiled. Foots oils are derived from deoiled slack waxes. Fischer-Tropsch waxes are prepared by the Fischer-Tropsch synthetic process.

[0010] The hydrocarbonaceous feedstocks used herein may also contain high concentrations of nitrogen and sulfur contaminants. Feeds containing up to 0.2 wt.% of nitrogen, based on the hydrocarbonaceous feedstock, and up to 3.0 wt.% of sulfur can be processed in the present process.

[0011] As discussed above, the hydrocarbonaceous feedstocks used herein are contacted with a hydrocracking catalyst under effective hydrocracking conditions to produce a hydrocracked product. Suitable hydrocracking catalysts

typically comprise at least one hydrogenation component. The hydrogenation component is preferably supported on a refractory support. Non-limiting examples of suitable refractory supports include two or more refractory oxides such as a silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid-treated clays, and the like. Acidic metal phosphates such as alumina-phosphate may also be used as refractory supports. Preferred refractory supports comprise composites of silica and alumina. Particularly preferred refractory supports are the partially dehydrated zeolitic crystalline molecular sieves of the X or Y crystal type, having relatively uniform pore diameters of about 8-14 Angstroms and comprising silica, alumina, and one or more exchangeable zeolitic cations alone or in intimate mixture with other amorphous bases. These particularly preferred refractory supports typically contain from about 20 to about 100 weight percent zeolite.

[0012] Typically, the hydrogenation components are present upon the refractory support in an amount from about 0.3 to about 25 wt.%. By “on support” we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g. then 20 wt.% Group VIII metal would mean that 20 g. of Group VIII metal was on the support. Suitable hydrogenation components are selected from Group VIB metals, Group VIII metals, their oxides, or mixtures thereof. Non-limiting examples of suitable hydrogenation components comprise the oxides of chromium, tungsten, cobalt, nickel, or the corresponding free metals, or any combination thereof. The oxides of other transition metals, such as, for example, rhenium, can also be used as a hydrogenation component. Preferred hydrogenation components are platinum, palladium, rhodium or iridium.

[0013] As used herein, effective hydrocracking conditions are to be considered temperatures in the range about 400°F to about 800°F, preferably

about 450°F to about 750°F. Total pressures between about 100 to about 1000 psig, preferably between about 200 to about 600 psig, hydrogen partial pressures between about 50 to about 450 psig, preferably about 150 to about 360 psig, and gas hourly space velocities (GHSV's) between about 200 to about 2000, preferably between about 500 to about 1500. Higher total pressures and higher hydrogen partial pressure can be utilized. Thus, the practitioner of the present invention may utilize any known hydrocracking catalyst known under any known hydrocracking conditions to produce a hydrocracked product.

[0014] The hydrocracked product is subsequently fractionated in a suitable fractionation tower. The fractionation tower used herein can be either a vacuum or atmospheric distillation tower. It is preferred to use a vacuum distillation tower. The temperatures at the bottom and top of the vacuum distillation tower can be any temperatures that allow the vacuum distillation process to effectively produce at least a first bottoms fraction, defined below. Preferably, the temperatures at the bottom and top of the vacuum distillation tower are about 585°F and 485°F respectively, more preferably about 575°F and 475°F, respectively. Vacuum pressures suitable for use herein can be any pressures that when used allow the vacuum distillation tower to effectively produce at least a first bottoms fraction. Preferably, the vacuum distillation tower pressure is 45-60 psig (vacuum), most preferably 50-55 psig (vacuum). It should be noted that by first bottoms fraction it is meant that fraction having the higher boiling point from the fractionation tower.

[0015] The first bottoms fraction so produced typically has a mid-boiling point range (50% LV), as determined by ASTM D6417 of about 350°C to about 450°C, preferably from about 375°C to 430°C and the first bottoms stream has a mid-boiling point range greater than 430°C to about 575°C, more preferably from about 460°C to about 525°C. The viscosity of the first bottoms fraction

ranges from about 200 SUS at 100°F to about 300 SUS at 100°F, 200 SUS at 100°F to about 275 SUS at 100°F, more preferably 225 SUS at 100°F to about 275 SUS at 100°F.

[0016] After the hydrocracked product has been fractionated, the above-defined first bottoms fraction thus produced is contacted with an extraction solvent to produce at least an aromatics-rich extract solution and an aromatics-lean raffinate solution. The extraction solvent used herein can be any extraction solvent known that has an affinity for aromatic hydrocarbons in preference to non-aromatic hydrocarbons. Non-limiting examples of such extraction solvents include sulfolane, furfural, phenol, and N-methyl pyrrolidone ("NMP"). Furfural, phenol, and NMP are preferred.

[0017] The first bottoms fraction can be contacted with the extraction solvent by any suitable solvent extraction method. Non-limiting examples of suitable solvent extraction methods include batch, semi-batch, or continuous. It is preferred that the extraction process be a continuous process, and it is more preferred that the continuous process be operated in a counter-current fashion. In a counter-current configuration, it is preferred that the first bottoms fraction be introduced into the lower end of an elongated contacting zone or tower and caused to flow in an upward direction while the extraction solvent is introduced at the upper end of the tower and allowed to flow in a downward direction, counter-current to the upflowing first bottoms fraction. In this configuration, the first bottoms fraction is forced to pass counter-currently to the extraction solvent resulting in intimate contact between the extraction solvent and the first bottoms fraction. The extraction solvent and the first bottoms fraction migrate to opposite ends of the contacting zone.

[0018] The conditions under which the first bottoms fraction is contacted with the extraction solvent include tower top temperatures from about 180°F(82°C) to about 225°F(107°C), preferably from about 160°F(71°C) to about 205°F(96°C). Tower bottom temperatures are typically about 40°F, preferably 30°F, lower than the tower top temperatures. Pressures typically range from about 0psi(0kPa) to about 20psi(138kPa), preferably from about 5psi(34kPa) to about 15psi(103kPa). In a most preferred embodiment, the temperature and pressure are selected to prevent complete miscibility of the first bottoms fraction in the extraction solvent.

[0019] The contacting of the first bottoms fraction with the extraction solvent produces at least an aromatics-rich extract solution and an aromatics-lean raffinate solution. The aromatics-lean raffinate solution is then processed to remove at least a portion of the extraction solvent contained therein, thus producing an aromatics-lean raffinate. The removal of at least a portion of the extraction solvent can be done by any means known in the art effective at separating at least a portion of an extraction solvent from an aromatics-lean raffinate solution. Preferably the first aromatics-lean raffinate is produced by separating at least a portion of the extraction solvent from the first aromatics-lean raffinate solution in a stripping or distillation tower. By at least a portion, it is meant that at least about 80 vol.%, preferably about 90 vol.%, more preferably about 95 vol.%, based on the first aromatics-lean raffinate solution, of the extraction solvent is removed from the first aromatics-lean raffinate solution. Most preferably substantially all of the extraction solvent is removed from the aromatics-lean raffinate solution.

[0020] Although there are many suitable processes and methods available in the art for removing at last a portion of the extraction solvent from the first aromatics-lean raffinate solution, it is best accomplished by use of a distillation

tower. The distillation tower used preferably continuously and preferentially separates at least a portion of the extraction solvent from the hydrocarbon fraction present in the aromatics-lean raffinate solution. The temperatures at the bottom and top of the distillation tower can be any temperatures that allow the vacuum distillation to effectively separate at least a portion of the extraction solvent from the hydrocarbon fraction present in the aromatics-lean raffinate solution. Preferably, the temperatures at the bottom and top of the distillation tower are about 585°F and 485°F respectively, more preferably about 575°F and 475°F, respectively. Pressures suitable for use herein can be any pressures that when used allow the distillation tower to effectively separate at least a portion of the extraction solvent from the hydrocarbon fraction present in the aromatics-lean raffinate solution. Preferably, the vacuum distillation tower pressure is 45-60 psig, most preferably 50-55 psig. It is also preferred to recycle the recovered solvent to the start of the extraction process.

[0021] The aromatics-rich extract solution can be passed to further processing. However, it is preferred that the aromatics-rich extract solution be treated in the same manner as the aromatics-lean raffinate solution, i.e. be treated to remove at least a portion of the extraction solvent, to produce at least an aromatics-rich extract.

[0022] After at least a portion of the extraction solvent has been removed, the resulting aromatics-lean raffinate is dewaxed to produce a dewaxed product. The manner in which the aromatics-lean raffinate is dewaxed can be any suitable dewaxing method or process. Non-limiting examples of suitable dewaxing methods include catalytic and solvent dewaxing. Preferred is solvent dewaxing. In the solvent-dewaxing of the aromatics-lean raffinate, an effective amount of any suitable dewaxing solvent may be used, for example, between about 50 and about 700 vol.% solvent to oil ratio, most preferably between about 100 and 500

vol.% solvent to oil ratio may be used. Non-limiting examples of suitable dewaxing solvents include methyl ethyl ketone ("MEK") and methyl isobutyl ketone ("MIBK"). Preferred dewaxing solvents include a mixture of MEK and MIBK, preferred are those mixtures containing about 30 vol.% MEK, based on the total volume of the solvent.

[0023] After dewaxing, the dewaxed product is fractionated to produce at least a second bottoms fraction. The fractionation tower used to fractionate the dewaxed product can be either a vacuum or atmospheric distillation tower. It is preferred to use a vacuum distillation tower. The temperatures at the bottom and top of the vacuum distillation tower can be any temperatures that allow the vacuum distillation to effectively produce at least a second bottoms fraction, defined below. Preferably, the temperatures at the bottom and top of the distillation tower are about 585°F and 485°F respectively, more preferably about 575°F and 475°F, respectively. Vacuum pressures suitable for use herein can be any pressures that when used allow the vacuum distillation tower to effectively produce at least a second bottoms fraction. Preferably, the vacuum distillation tower pressure is 45-60 psig (vacuum), most preferably 50-55 psig (vacuum). It should be noted that by second bottoms fraction it is meant that fraction having the higher boiling point from the fractionation tower.

[0024] The second bottoms fraction so produced typically has a mid-boiling point range (50%LV) greater than 450°C to about 550°C, more preferably from about 460°C to about 525°C. The viscosity of the second bottoms fraction ranges from about 350 SUS at 100°F to about 650 SUS at 100°F, 400 SUS at 100°F to about 600 SUS at 100°F, more preferably 450 SUS at 100°F to about 550 SUS at 100°F.

[0025] As previously stated, the second bottoms fraction is hydrofinished under effective hydrofinishing conditions to produce at least one base oil. Hydrofinishing is a form of mild hydrotreating directed to saturating any lube range olefins and residual aromatics as well as to removing any remaining heteroatoms and color bodies. Thus, hydrofinishing the second bottoms fraction adjusts product qualities to desired specifications. Generally the hydrofinishing will be carried out under effective conditions including temperatures from about 150°C to about 350°C, preferably about 180°C to 250°C, total pressures from about 2859 to about 20786 kPa (about 400 to 3000 psig), liquid hourly space velocities ("LHSV") typically range from about 0.1 to 5 LHSV (hr^{-1}), preferably about 0.5 to about 3 hr^{-1} , and typical hydrogen treat gas rates range from about 44.5 to about 1780 m^3/m^3 (250 to 10000 scf/B).

[0026] The catalyst used in hydrofinishing the second bottoms fraction is typically a hydrotreating catalyst. Suitable hydrotreating catalysts for use in hydrofinishing the second bottoms fractions are any conventional hydrotreating catalyst and includes those which are comprised of at least one Group VIII metal, preferably Fe, Co and Ni, more preferably Co and/or Ni, and most preferably Co; and at least one Group VI metal, preferably Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. It is within the scope of the present invention that more than one type of hydrotreating catalyst be used in the same hydrofinishing reaction vessel. The Group VIII metal is typically present in an amount ranging from about 2 to 20 wt.%, preferably from about 4 to 12%. The Group VI metal will typically be present in an amount ranging from about 5 to 50 wt.%, preferably from about 10 to 40 wt.%, and more preferably from about 20 to 30 wt.%. All metals weight percents are on support. By "on support" we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g. then

20 wt.% Group VIII metal would mean that 20 g. of Group VIII metal was on the support.

[0027] The at least one base oil produced by the process according to the invention have very high viscosities and can be produced in high yields from the above-described feeds. The viscosities of the at last one base oil typically fall within the range described above for the second bottoms fraction. Thus, the at least one base oil typically has a mid-boiling point range (50%LV) greater than 450°C to about 550°C, more preferably from about 460°C to about 525°C. The viscosity of the at least one base oil ranges from about 350 SUS at 100°F to about 650 SUS at 100°F, 400 SUS at 100°F to about 600 SUS at 100°F, more preferably 450 SUS at 100°F to about 550 SUS at 100°F.

[0028] The above description is directed at preferred embodiments of the present invention and it is not intended to limit the invention thereto. One having ordinary skill in the art will recognize that there are modifications and variations that are still within the spirit and scope of the present invention. The inventors herein contemplate any such variations and modifications and contemplate to cover such variations and modifications within the true spirit and scope of the present invention with the attached claims.

[0029] The following example will be useful in better illustrating the practice of the present invention, but is not meant to limit the invention.

EXAMPLE

[0030] A base oil was produced according to the above-described invention. A feedstock having a mid-boiling point of about 450°C was hydrocracked over a commercial hydrocracking catalyst marketed under the name HCY-642 to produce a hydrocracked product. The hydrocracked product was then

fractionated in a vacuum fractionation tower under conditions selected to yield about 10vol.% of a bottoms fraction having a mid-boiling point range (50% LV), as determined by ASTM D6417, greater than 450°C, preferably from 476°C, and a viscosity of about 11.1 cSt or more at 100°F. This bottoms fraction was then solvent extracted using phenol (0.5-1.5% water) and a 205°F tower top temperature and 170°F tower bottom temperature. The stripping medium was then removed using a vacuum stripping tower, thus producing an aromatics-lean raffinate. The aromatics lean raffinate was then solvent dewaxed using methyl ethyl ketone/methyl isobutyl ketone (30 vol% MEK/70 vol% MIBK) under conditions including 4:1 v/v solvent/oil and -15°C. The dewaxing solvent was then removed through the use of a vacuum stripping tower to produce a dewaxed product. The dewaxed product was then fractionated in a vacuum fractionation tower under conditions sufficient to produce 15vol.% of a second bottoms fraction having the properties defined below in Table 1. The second bottoms fraction was then hydrofined using a commercial catalyst marketed under the name C-411 under conditions including temperatures of about 280°C, 400 psi Hydrogen, 4 v/v space velocity. The results of this experiment are shown in Table 1 below.

Table 1

	Dewaxed Product	15 vol% second bottoms fraction, pre-hydrofining	15 vol% second bottoms fraction, post-hydrofining
Kinematic viscosity			
cSt at 40°C	44.54	96.63	96.57
cSt at 100°C	7.05	11.67	11.83
Viscosity, SUS at 100°F	231	502	501
Viscosity Index	117	110	112
Pour point, °C (D97)	-12	-15	-15